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## Report Title

Final Report: International Technical Exchange on 2D Atomic Sheets: Optoelectronics, Strain, and Energy Applications

### ABSTRACT

The 2D technical exchange was well attended with leading researchers from across the world providing progress updates and perspectives on 2D materials for defense science and technology. There were more than 100 participants, 23 invited talks, and more than 10 poster sessions. A consensus conclusion from the meeting is that 2D materials have a wide potential to fulfill army needs in the long-term. In the short-term, much progress is needed in scalable material synthesis. Overcoming this challenge will pave the way for practical applications.

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**Sub Contractors (DD882)**

## **Inventions (DD882)**

## **Scientific Progress**

## **Technology Transfer**

Substantial technology transfer involving ARL scientists was achieved. this has led to several ongoing collaborations between ARL scientists and leading nanomaterial researchers to benefit Army technology

# ARO 2014 2D International Technical Exchange Final Report

**Principal Investigator:** Dr. Deji Akinwande, University of Texas – Austin

Event Information	
<b>Event Title.</b> Technical Exchange on 2D Atomic Sheets: Optoelectronics, Strain, and Energy Applications	
<b>Event Organizer/Chair:</b> Deji Akinwande, University of Texas - Austin	
<b>Event Location:</b> Army Research Laboratory (ARL), Adelphi, MD, USA	
<b>Location Coordinator:</b> Dr. Madan Dubey	
<b>Start Date:</b> 8/12/2014	<b>End Date:</b> 8/13/2014
<b>Topic Areas or Themes:</b> i. Electronics. ii. Photonics. iii. Engineering Strain. iv. Power and Energy.	

The 2D technical exchange was well attended with leading researchers from across the world providing progress updates and perspectives on 2D materials for defense science and technology. There were more than 100 participants, 23 invited talks, and more than 10 poster sessions. A consensus conclusion from the meeting is that 2D materials have a wide potential to fulfill army needs in the long-term. In the short-term, much progress is needed in scalable material synthesis. Overcoming this challenge will pave the way for practical applications.

The event agenda is listed below followed by the talk titles and abstracts of the invited speakers.

## Event Agenda

Time	Day 1 (August 12)
<b>Morning Session</b>	<b>Materials</b>
<b>7:45 – 8:45 am</b>	Registration and Breakfast
<b>8:45 – 9:10 am</b>	Welcome and Introductory Remarks Deji Akinwande, Chair, 5mins Madan Dubey, ARL Host – 5mins Philip Perconti, Director, Sensors and Electron Devices Directorate, ARL -15mins
<b>9:15 – 9:40 am</b>	<b>Andrea Ferrari</b> , University of Cambridge, UK Keynote: Raman Spectroscopy in Layered Materials
<b>9:45 – 10:05 am</b>	<b>Manish Chhowalla</b> , Rutgers University <i>Phase Engineering in 2D Transition Metal Dichalcogenides</i>
<b>10:10 – 10:30 am</b>	<b>Guy Le Lay</b> , Aix Marseille Université, France <i>Silicene and germanene : synthetic cousins of graphene</i>
<b>10:35 – 10:55 am</b>	<b>Josh Goldberger</b> , Ohio State University <i>Group IV Graphene Analogues</i>
<b>11:00 – 11:20 am</b>	<b>Peide Ye</b> , Purdue University <i>Semiconducting Black Phosphorus and Phosphorene for Electronic and Optoelectronic Applications</i>
<b>11:25 – 11:45 am</b>	<b>Li Shi</b> , University of Texas - Austin <i>Thermal and Thermoelectric Properties and Applications of Two-Dimensional Materials beyond Graphene</i>
<b>11:45 – 1:15 pm</b>	Lunch and Poster session
<b>Afternoon Session</b>	<b>Electronics – Session Chair, Ron Polcawich, ARL</b>

<b>1:15 – 1:25 pm</b>	Remarks About ARO Basic Research Programs Pani Varanasi, Program Manager, Materials Science Division, ARO
<b>1:30 – 1:55 pm</b>	<b>Frank Schwierz</b> , TU-Ilmenau, Germany Keynote: <i>2D Materials Beyond Graphene for More Moore and More Than Moore Application</i>
<b>2:00 – 2:20 pm</b>	<b>James Hone</b> , Columbia University <i>MoS<sub>2</sub>: Piezoelectric response and high low-T mobility</i>
<b>2:25 – 2:45 pm</b>	<b>Sayeef Salahuddin</b> , UC-Berkeley <i>Electronics and Optoelectronics Using 2D Dichalcogenides</i>
<b>2:50 – 3:10 pm</b>	<b>Evan Reed</b> , Stanford University <i>Phase Change Properties and Strain Engineering in 2D Materials</i>
<b>3:15 – 3:35 pm</b>	<b>Emanuel Tutuc</b> , University of Texas - Austin <i>Electron Interaction and Tunneling in Graphene-based Heterostructures</i>
<b>3:40 – 4:00 pm</b>	<b>Deji Akinwande</b> , University of Texas - Austin <i>Ubiquitous and Flexible 2D Nanoelectronics: Are the materials there yet?</i>
<b>4:10 – 5:00 pm</b>	Open Technical Exchange and Tour of ARL facilities

Time	Day 2 (August 13)
<b>Morning Session</b>	<b>Optoelectronics</b>
<b>7:45 – 8:45 am</b>	Registration and Breakfast
<b>8:45 – 9:10 am</b>	<b>Tony Heinz</b> , Columbia University Keynote: <i>Electronic and Optical Properties of Atomically Thin Transition Metal Dichalcogenides</i>
<b>9:15 – 9:35 am</b>	<b>Michael Strano</b> , MIT <i>Understanding the stacking number dependence of optoelectronic properties for MoS<sub>2</sub> and its junction with graphene</i>
<b>9:40 – 10:00 am</b>	<b>Mathias Steiner</b> , IBM, Brazil <i>Optoelectronic devices with layered 2D materials: light generation and photo-detection</i>
<b>10:05 – 10:25 am</b>	<b>Andres Castellanos-Gomez</b> , TU-Delft, Netherlands <i>Atomically thin optoelectronics: 2D semiconductors beyond graphene</i>
<b>10:30 – 10:45 am</b>	Break (15 mins)
	<b>Energy Properties – Session Chair, Chris Morris, ARL</b>
<b>10:45 – 11:05 am</b>	<b>Cinzia Casiraghi</b> , University of Manchester, UK <i>Light-Matter Interactions in Heterostructures of Atomically Thin Films</i>
<b>11:10 – 11:30 am</b>	<b>Eric Pop</b> , Stanford University <i>Thermal and Energy Applications of 2D Materials and Stacks</i>
<b>11:35 – 11:55 am</b>	<b>Chris Hinkle</b> , University of Texas - Dallas <i>Transition Metal Dichalcogenide Growth and Characterization for Low-power Electronics and Energy Storage</i>
<b>12:00 – 1:30 pm</b>	Lunch and Poster session

<b>Afternoon Session</b>	<b>Interfaces and Sensors – Session Chair, Chris Morris, ARL</b>
<b>1:30 – 1:55 pm</b>	<b>Ya-Hong Xie, UCLA</b> Keynote: <i>van der Waals materials research at STARnet FAME Center</i>
<b>2:00 – 2:20 pm</b>	<b>Vivek Shenoy, University of Pennsylvania</b> <i>Strain engineering of the electronic structure of 2D materials</i>
<b>2:25 – 2:45 pm</b>	<b>Ert Cubukcu, University of Pennsylvania</b> <i>Opto-electro-mechanical devices and sensors with 2D materials</i>
<b>2:50 – 3:10 pm</b>	<b>Ted Norris, University of Michigan</b> <i>Multilayer structures of graphene and 2D materials - Electron Dynamics and Applications</i>
<b>3:15 – 3:30 pm</b>	<b>Closing Remarks</b> <b>Deji Akinwande, Chair</b> <b>Madan Dubey, ARL Host</b>

## Invited Talk Titles and Abstracts

### Phase Engineering in 2D Transition Metal Dichalcogenides

Manish Chhowalla

Rutgers University

Two-dimensional transition metal dichalcogenides (2D TMDs) — whose generalized formula is  $MX_2$ , where M is a transition metal of groups 4–7 and X is a chalcogen — exhibit versatile chemistry and consist of a family of over 40 compounds that range from complex metals to semiconductors to insulator. Complex metal TMDs assume the 1T phase where the transition metal atom coordination is octahedral. The 2H phase is stable in semiconducting TMDs where the coordination of metal atoms is trigonal prismatic. We have been studying the 1T phase in *semiconducting* TMDs. In particular, we have focused on mechanisms involved in inducing the meta-stable 1T phase, kinetics of phase transformation and fundamental structural and electronic properties. We have implemented phase-engineered materials as hydrogen evolution reaction (HER) catalysts and as low resistance contact electrodes in electronic devices. We have also exploited the metallic nature of the 1T phase to functionalize a variety of TMDs. The attachment of functional groups leads to dramatic changes in the opto-electronic properties of the material.

### Silicene and germanene : synthetic cousins of graphene

Guy Le Lay

Aix-Marseille University, PIIM-CNRS, Marseille, France

Silicene and germanene are novel artificial two-dimensional allotropes of elemental silicon and germanium and new counterparts of graphene. The mobilities of their charge carriers are expected to be very high and they are predicted to be robust two-dimensional topological insulators. After describing our fabrication of epitaxial single and multilayer silicene on silver (111) substrates [1], I will present the synthesis of epitaxial germanene on Au(111) [2]. I will further review fundamental results on these novel two-dimensional materials and anticipate potential applications.

[1] P. Vogt et al., Phys. Rev. Lett., **108**, 155501 (2012); P. Vogt et al., Appl. Phys. Lett., **104**, 021602 (2014).

[2] M. E. Davila et al., submitted

## **2D Materials Beyond Graphene for More Moore and More Than Moore Application**

Frank Schwierz

Fachgebiet Festkörperelektronik, Technische Universität Ilmenau, Ilmenau, Germany

2D materials beyond graphene have found significant interest in the electronic device community recently and their use as channel material for field-effect transistors is hotly debated. In the present talk, we provide a condensed overview on the 2D materials beyond graphene and discuss potential applications of 2D transistors in the More Moore and More Than Moore domains of semiconductor electronics. Special emphasis is put on the prospects of 2D materials for digital electronics. We show that in the near and medium term an implementation of 2D materials into digital CMOS is rather unlikely. On the other hand, the situation may change in the long term. In 5-nm and below CMOS generations, 2D materials have realistic chances to play an important role. Furthermore, the BiSFET as a novel switching device concept is introduced. Finally, the application of 2D transistors in the More Than Moore domain (RF, flexible, printable, and transparent electronics) is briefly discussed.

### **“Optoelectronic devices with layered 2D materials: light generation and photo-detection”**

Mathias Steiner, IBM Research

#### **Abstract**

Two-dimensional (2D) layered semiconductors, such as molybdenum disulfide and black phosphorus, are researched in view of their potential application in novel optoelectronics technologies. From a device perspective, electrical light generation and photo-detection in the embedded 2D materials are key physical effects that need to be investigated. In the first part of this presentation, I will report on electroluminescence experiments in single layer molybdenum disulfide [1] and discuss strategies for improving efficiency and control of electrically excited light emission in 2D materials. In the second part of this presentation, I will show how a black phosphorus device can be used as a point-like photo-detector in the visible and near-IR spectral range for acquiring diffraction-limited images that exhibit sub-micron features [2]. Finally, I will briefly discuss promising optoelectronic functionalities and applications based on layered 2D semiconductors.

[1] “Electroluminescence in Single Layer MoS<sub>2</sub>”, R. S. Sundaram, M. Engel, A. Lombardo, R. Krupke, A. C. Ferrari, Ph. Avouris, M. Steiner, Nano Letters 13, 1416 (2013)

[2] “A black phosphorus photo-detector for multispectral, high-resolution imaging” M. Engel, M. Steiner, Ph. Avouris, arXiv:1407.2534 (2014)

## Atomically thin optoelectronics: 2D semiconductors beyond graphene

Andres Castellanos-Gomez

*Delft University of Technology, 2628 CJ Delft, The Netherlands*

\*E-mail: [a.castellanosgomez@tudelft.nl](mailto:a.castellanosgomez@tudelft.nl)

In this talk I will review the recent progress on the application of atomically thin crystals different than graphene on optoelectronic devices. The current research of 2D semiconducting materials has already demonstrated the potential of this family of materials in optoelectronic applications [1-3]. Nonetheless, it has been almost limited to the study of molybdenum- and tungsten- based dichalcogenides (a very small fraction of the 2D semiconductors family). Single layer molybdenum and tungsten chalcogenides present large direct bandgaps ( $\sim 1.8$  eV). Alternative 2D semiconducting materials with smaller direct bandgap would be excellent complements to the molybdenum and tungsten chalcogenides as they could be used for photodetection applications in the near infrared. Furthermore, for applications requiring a large optical absorption it would be desirable to find a family of semiconducting layered materials with direct bandgap even in their multilayer form.

Here I will summarize the recent results on the exploration of novel 2D semiconducting materials for optoelectronic applications: black phosphorus [4-6],  $\text{TiS}_3$  [7]. Recent efforts towards tuning the optoelectronic properties of 2D semiconductors by strain engineering will be also discussed [8]. The talk will conclude with an outlook section where the potential of these novel 2D materials on 'real life' optoelectronic devices will be discussed.

### References

- [1] Yin Z. et al, *Single-layer MoS<sub>2</sub> phototransistors*, ACS Nano (2011)
- [2] Lopez-Sanchez, O., et al., *Ultrasensitive photodetectors based on monolayer MoS<sub>2</sub>*, Nature Nanotech. (2013)
- [3] Buscema M., et al., *Large and tunable photo-thermoelectric effect in single-layer MoS<sub>2</sub>*, Nano Letters (2013)
- [4] Castellanos-Gomez, A., et al., *Isolation and Characterization of few-layer black phosphorus*. 2D Materials (2014)
- [5] Buscema M., et al., *Fast and broadband photoresponse of few-layer black phosphorus field-effect transistors*. Nano Letters (2014)
- [6] Buscema M., et al., *Photovoltaic effect in few-layer black phosphorus PN junctions defined by local electrostatic gating*. Nature Communications (2014).
- [7] Island J.O., et al., *Ultrahigh photoresponse of atomically thin TiS<sub>3</sub> nanoribbon transistors*. Adv. Opt. Mater. (2014)
- [8] Castellanos-Gomez, A., et al., *Local strain engineering in atomically thin MoS<sub>2</sub>*. Nano Letters (2013)

# Electron Interaction and Tunneling in Graphene-based Heterostructures

Emanuel Tutuc

*Microelectronics Research Centers, The University of Texas at Austin,  
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## Abstract

Vertical heterostructures consisting of atomic layers separated by insulators can enable novel tunneling devices, and also open a window to explore electron interaction effect in these materials, otherwise not accessible in single layer devices. In this presentation we discuss two examples of vertical heterostructures of atomic layer materials, where electron interaction plays a key role.

We examine the electron transport in graphene-MoS<sub>2</sub> heterostructures, fabricated using a layer-by-layer transfer approach. Four point conductivity measurements of the heterostructure as a function of back-gate bias show ambipolar characteristics, with a clear conductivity saturation on the electron branch. Magnetotransport measurements reveal that the conductivity saturation marks the onset of MoS<sub>2</sub> being populated with electrons. Most surprisingly, once the MoS<sub>2</sub> becomes populated with electrons the carrier density in graphene decreases with increasing gate bias, a finding indicating that the MoS<sub>2</sub> electrons have a negative quantum capacitance [1].

A second type of heterostructure examined here are double bilayer heterostructures, consisting of two bilayer graphene flakes separated by hexagonal boron-nitride. Using the top layer as a resistively detected Kelvin probe we map the chemical potential of the bottom bilayer graphene as a function of electron density, perpendicular magnetic field, and transverse electric field. At zero magnetic field the chemical potential reveals a strongly non-linear dependence on density, with an electric field induced energy gap at charge neutrality. The data allow a direct measurement of the electric field-induced bandgap at zero magnetic field, the orbital Landau level energies, and the broken symmetry quantum Hall state gaps at high magnetic fields [2]. The interlayer transport shows a gate tunable negative differential resistance suggestive of momentum conserving tunneling.

## References

- [1] S. Larentis, *et al.*, “Band Offset and Negative Compressibility in Graphene-MoS<sub>2</sub> Heterostructures”, *Nano Letters* **14**, 2039 (2014).
- [2] K. Lee, *et al.*, “Chemical potential and quantum Hall ferromagnetism in bilayer graphene mapped using double bilayer heterostructures”, *Science* **345**, 58 (2014).

## **Thermal and Thermoelectric Properties and Applications of Two-Dimensional Materials beyond Graphene**

Li Shi

Department of Mechanical Engineering and Texas Materials Institute  
The University of Texas at Austin, Austin, Texas 78712

Besides the switching speed and on-off ratio, the hot spot temperature is one important performance metric of novel electronic devices fabricated from two-dimensional (2D) materials beyond graphene. This performance metric depends sensitively on the largely unknown thermal and thermoelectric properties of various 2D materials. Following our prior works on thermal transport measurements of graphene, we have recently studied thermal and thermoelectric properties of few-layer h-BN, MoS<sub>2</sub>, germanane, and bismuth telluride. The results reveal that surface perturbation suppresses the in-plane lattice thermal conductivity of these 2D materials. The thickness needed for recovery to the bulk lattice thermal conductivity scales with the bulk phonon mean free path. In addition, we have observed decrease in both the electrical conductivity and thermal conductivity with decreasing thickness of bismuth telluride nanoplates. Based on the understanding of these size-dependent, environment-sensitive thermal and thermoelectric properties, we have explored the use of h-BN thin layers and continuous foam architectures of ultrathin graphite and h-BN as heat spreaders in flexible electronic devices and for thermal management of energy storage devices.

## **Light-Matter Interactions in Heterostructures of Atomically Thin Films**

Cinzia Casiraghi

School of Chemistry, University of Manchester (UK)

The isolation of various two-dimensional (2D) materials, and the possibility to combine them in vertical stacks, has created a new paradigm in materials science: heterostructures based on 2D crystals. Such a concept can be used to focus on particular phenomena or for specific applications.

In this talk I will show that layering sheets of graphene and hexagonal boron nitride (hBN), molybdenum disulfide (MoS<sub>2</sub>), or tungsten disulfide (WS<sub>2</sub>) allow operation of tunnelling transistors [1,2] and efficient flexible photovoltaic devices with external quantum efficiency of above 30% [3]. Furthermore, I will show that graphene placed on hexagonal-Boron Nitride (h-BN) experiences a superlattice potential, which leads to a strong reconstruction of graphene's electronic spectrum [4,5]. Raman spectroscopy is found to allow high-throughput and non-destructive identification of graphene/hBN superlattices [6], making this technique a fundamental tool in the fabrication of superlattice based-devices.

In the last part of this talk I will show that heterostructures can also be assembled from chemically exfoliated 2D crystals [7], allowing for low-cost and scalable methods to be used in heterostructures fabrication [8].

1. Georgiou et al, Nat. Nanotechnol. 8, 100 (2013)
2. Britnell et al, Science 335, 947 (2012)
3. Britnell et al, Science 340, 1311-1314 (2013)
4. Wallbankey al, Phys. Rev. B87, 245408 (2013)

5. Ponomarenko et al, Nature 497, 594 (2013)
6. Eckmann et al, Nano Lett. 13 (11), 5242 (2013)
7. Yang et al, 2D Materials, 1, 011012 (2014)
8. Whiters et, al Nano Letters, 14, 3987 (2014)

## **Raman Spectroscopy in Layered Materials**

Andrea C. Ferrari

(Cambridge Graphene Centre, Cambridge, 9 JJ Thomson Avenue, Cambridge CB3 0FA, UK)

Graphene and other two-dimensional crystals can be combined to form various hybrids and heterostructures, creating "materials on demand" with properties determined by the interlayer interaction. This is the case even for a single material, where multilayer stacks with different relative orientation have different optical and electronic properties. Probing and understanding the interface coupling is thus of primary importance for fundamental science and applications. Raman spectroscopy is an integral part of graphene research[1-3]. The Raman spectrum of graphite and few layer graphene consists of two fundamentally different sets of peaks. Those, such as D, G, 2D, etc, present also in a monolayer, and due to in-plane vibrations[1-3], and others, such as the shear (C) modes[3,4] and the layer breathing (LB) modes (LBMs)[3-9], due to relative motions of the planes themselves, either perpendicular or parallel to their normal. This is general for any layered material, where similar C and LB modes exist[7], a direct probe of interlayer interactions. I will overview the current understanding of C and LB modes in layered materials and show how these are "universal" and provide an unified approach to investigate any layered material, be it composed or carbon atoms or not. This paves the way to the use of Raman spectroscopy as a primary tool to uncover the interface coupling of two-dimensional hybrids and heterostructures[8].

1. A. C. Ferrari et al. Phys. Rev. Lett **97**, 187401 (2006)
2. A. C. Ferrari et al. Solid State Comm. **143**, 47 (2007)
3. A. C. Ferrari, D. M. Basko Nature Nanotech. **8**, 235 (2013)
4. P. H. Tan et al. Nature Materials **11**, 294 (2012)
5. C. Lui et al. Nano Lett. **2**, 5539 (2012)
6. K. Sato et al. Phys. Rev. B **84**, 035419 (2011)
7. X. Zhang et al. Phys. Rev. B **87**, 115413 (2013)
8. J. B. Wu et al. submitted (2014)

## **Seminar Title: Group IV Graphane Analogues**

Joshua Goldberger

Ohio State University

Abstract:

Graphene's success has shown that it is not only possible to create stable, single-atom thick sheets from a crystalline solid, but that these materials have fundamentally different properties than the parent material. Here we will describe our recent success on the synthesis, properties, and applications of Group IV graphane analogues. We have synthesized for the first time, mm-scale crystals of a hydrogen-terminated germanium multilayered graphane analogue (germanane, GeH) from the topochemical deintercalation of  $\text{CaGe}_2$ . This layered van der Waals solid is analogous to multilayered graphane. We demonstrate that it is possible to covalently terminate the external surface with organic substituents to tune the electronic structure, and enhance the stability. These materials represent a new class of covalently terminated graphane analogues having great potential for a wide range of optoelectronic and sensing applications, especially since theory predicts a direct band gap of 1.53 eV and an electron mobility of  $18,000 \text{ cm}^2/\text{Vs}$  which is five times higher than that of bulk Ge.

## **Electronic and Optical Properties of Atomically Thin at Transition Metal Dichalcogenides**

Tony F Heinz

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In this paper, we will discuss recent advances in the study of atomically thin layers of transition metal dichalcogenides, such as  $\text{MoS}_2$ , as revealed by optical spectroscopy. Although the structure of the monolayer of  $\text{MoS}_2$  is similar to that of graphene, the A and B sublattice are occupied either by Mo atoms or by a pair of S atoms, rather than just by C atoms. This difference in symmetry allows  $\text{MoS}_2$  to be a semiconductor with a significant band gap. Through characterization of the optical properties of the material as a function of thickness, we show that quantum confinement effects lead to a crossover in  $\text{MoS}_2$  from an indirect gap semiconductor in the bulk to a direct gap semiconductor at monolayer thickness.

As expected for lower-dimensional materials, Coulomb interactions and excitonic effects are very strong in monolayer  $\text{MoS}_2$ . Recent spectroscopic studies of the exciton Rydberg states in  $\text{WS}_2$  reveal a binding energy in excess of 300 meV, as well as an anomalous energy level structure. Both the high binding energy and the unusual energy level structure of the excited excitonic states reflect the weakened dielectric screening experienced by charges separated by a length scale great than the layer thickness. These same strong excitonic interactions also give rise charged exciton with binding energies sufficient to produce stable bound states even at room temperature.

Another distinctive feature of this class of materials is the possibility of creating long-lived valley polarization in which one of the two inequivalent, but energetically degenerate, K and K' valleys is populated in preference to the other. We demonstrate how this can be achieved using optical

excitation with circularly polarized radiation and monitored through the retention of the polarization in fluorescence emission. We also show that pronounced changes in symmetry from the non-centrosymmetric monolayer to the centrosymmetric bilayer are reflected both in the second-order nonlinear optical response of the materials and in the production of valley polarization by circularly polarized radiation.

## **Transition Metal Dichalcogenide Growth and Characterization for Low-power Electronics and Energy Storage**

Prof. Christopher Hinkle, Department of Materials Science and Engineering,

University of Texas at Dallas

We will discuss our promising studies demonstrating the growth of novel transition metal dichalcogenides (TMDs) that will enable a variety of new heterostructures for next-generation low-power devices and high energy density Li-ion battery electrodes. We will focus this talk on the growth of HfSe<sub>2</sub>, an interesting candidate as the drain material for broken-gap tunnel FETs and Li-ion battery anodes with high electronic conductivity. We will discuss the growth of high-quality HfSe<sub>2</sub> thin films by molecular beam epitaxy (MBE) on a variety of substrates and discuss how the crystal quality changes as a function of substrate properties with the best growth results obtained on inert, hexagonal symmetry surfaces such as graphene and MoS<sub>2</sub>. HfSe<sub>2</sub> thin films on highly ordered pyrolytic graphite (HOPG), for example, show an atomically sharp interface between the HfSe<sub>2</sub> and HOPG with preferred orientation as characterized by RHEED, STM, TEM, XPS, Raman, and XRD with measured properties consistent with the theoretical predictions of the 1-T phase. We will discuss the impact of lattice mismatch and growth temperature on the film quality and surface reactivity upon atmospheric exposure. We will also discuss our recent studies of intrinsic defects in TMDs and their impact on material and device variability, particularly their influence on Schottky contacts.

## **MoS<sub>2</sub>: Piezoelectric response and high low-T mobility.**

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### **Abstract**

In the bulk, MoS<sub>2</sub> is centro-symmetric due to anti-alignment of adjacent layers. In the limit of one layer (or a small odd number of layers) this symmetry is broken and a strong piezo-electric response is expected. We have measured piezo-electric and response of MoS<sub>2</sub>, and find the expected strong response for 1,3, and 5 –layer samples, and no response for 2 and 4-layer (and bulk) material. The response reverses sign when the strain direction is rotated by 90 degrees, as expected.

We have developed techniques to controllably ‘stack’ graphene on insulating hexagonal boron nitride, which dramatically reduces disorder and increases electronic mobility. We have recently extended these techniques to MoS<sub>2</sub>, to achieve multi-terminal contact to BN-encapsulated MoS<sub>2</sub>. These devices show very high mobility, up to above 30,000 cm<sup>2</sup>/Vs, at low T and strong SdH oscillations in high magnetic fields.

## **Semiconducting Black Phosphorus and Phosphorene for Electronic and Optoelectronic Applications**

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Phosphorus is one of the most abundant elements preserved in earth, constructing with a fraction of ~0.1% of the earth crust. In general, phosphorus has several allotropes. The two most commonly seen allotropes, white and red phosphorus, are widely used in explosives and safety matches. In addition, black phosphorus, though rarely mentioned, is a layered semiconductor and has great potentials in optical and electronic applications. Remarkably, this layered material can be reduced to one single atomic layer in the vertical direction owing to the van der Waals structure, known as phosphorene, where the physical properties can be tremendously different from its bulk counterpart. In this talk, we trace back to the 100 years research history on black phosphorus and extend the topic from black phosphorus to phosphorene. The physical and transport properties are highlighted, aiming at further applications in electronic and optoelectronics devices.

## **Phase Change Properties and Strain Engineering in 2D Materials**

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Two-dimensional Mo- and W-dichalcogenide compounds have a form that differs from graphene in an important respect: they can potentially exist in more than one crystal structure. Some of these monolayers exhibit hints of a poorly understood structural metal-to-insulator transition with the possibility of long metastable lifetimes. If controllable, such a transition could bring an exciting new application space to monolayer materials. Here we discover that mechanical deformations provide a route to switching thermodynamic stability between a semiconducting and a metallic crystal structure in these monolayer materials.<sup>1</sup> Based on hybrid range-limited density functional calculations including vibrational energy corrections, we discover that MoTe<sub>2</sub> is an excellent candidate phase change material. We identify a range from 0.3 to 3% for the tensile strains required to transform MoTe<sub>2</sub> under uniaxial conditions at room temperature. The potential for mechanical phase transitions is predicted for all six studied compounds.

In the second part of this talk, I will explore a new approach for strain engineering in monolayer materials using lithographically or otherwise patterned adatom adsorption.<sup>2</sup> These results show potential to generate strain states larger than those achievable using flexible substrate approaches. Under some circumstances, an annular adsorption pattern generates homogeneous tensile strains of approximately 2% in graphene inside an annular adsorption region, or approximately 30% of the strain in the adsorbed region. We find that an elliptical adsorption pattern produces strains of as large as 5%, close to the strain in the adsorbed region. Also, non-zero maximum shear strain

(~ 4%) can be introduced by an elliptical adsorption pattern. We find that an elastic plane stress model provides qualitative guidance for strain magnitudes and conditions under which buckling can be avoided. We identify geometric conditions under which this effect has potential to be scaled to larger areas without buckling.

### **Strain engineering of the electronic structure of 2D materials**

Vivek Shenoy, UPenn, School of Engineering and Applied Sciences

2D materials have received a lot of attention in the past few years for their superior electronic, optical, and thermal properties. Many of these properties depend on the geometrical structure, and can be altered by strain/deformation. Deformations can be caused by various factors, including thermal effects, mismatch with substrates, chemical functionalization as well as defects that arise during growth or processing. In this talk I will discuss how strain can be used to engineer the optoelectronic properties of 2D materials. I will show how strain can lead to direct to indirect transitions and metal to insulator transitions in different polytypes of transition metal dichalogenides and to novel topological insulating phases with unique electronic properties in functionalized germanane. I will also discuss progress in modeling the growth of 2D materials through chemical vapor deposition.

### **Understanding the stacking number dependence of optoelectronic properties for MoS<sub>2</sub> and its junction with graphene.**

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Atomically thin MoS<sub>2</sub> is of great interest for electronic and optoelectronic applications because of its unique two-dimensional (2D) quantum confinement, however, the scaling of optoelectronic properties of MoS<sub>2</sub> and its metallic junctions with layer number remains unaddressed. In this work, we utilize photocurrent spectral atomic force microscopy (PCS-AFM) to image the current and photocurrent generated between a biased PtIr tip and MoS<sub>2</sub> between  $n = 1$  to 10 layers. Dark current measurements in both forward and reverse bias reveal characteristic diode behavior well described by Fowler-Nordheim tunneling with a monolayer barrier energy of 0.605 eV and an effective barrier scaling linearly with layer number. Under illumination at 600 nm, the photocurrent response shows a marked decrease up to  $n = 4$  but increasing thereafter, which we describe using a model that accounts for the linear barrier increase at low  $n$ , but increased light absorption at larger layer number creating a minimum at  $n = 4$ . Comparative 2D Fourier analysis of physical height and photocurrent images shows high frequency spatial variations in substrate/MoS<sub>2</sub> contact that exceed the frequencies imposed by the ITO substrates. These results should aid in the design and understanding of optoelectronic devices based on quantum confined MoS<sub>2</sub>. We also studied MoS<sub>2</sub>-graphene heterostructures as a means of combining the advantages of high carrier mobility in graphene with the permanent band gap of MoS<sub>2</sub>. We report the electron transfer,

photoluminescence, and gate-controlled carrier transport in such heterostructures, showing that the junction behaves as a Schottky barrier, whose height can be artificially controlled by gating or doping graphene. When the applied gate voltage (or the doping level) is zero, the photoexcited electron hole pairs in monolayer MoS<sub>2</sub> can be split by the heterojunction, significantly reducing the photoluminescence. By applying negative gate voltage (or p-doping) in graphene, the interlayer impedance formed between MoS<sub>2</sub> and graphene exhibits a 100-fold increase. For the first time, we show that the gate-controlled interlayer Schottky impedance can be utilized to modulate carrier transport in graphene, significantly depleting the hole transport, but preserving the electron transport. Accordingly, we demonstrate a new type of FET device, which enables a controllable transition from NMOS digital to bipolar characteristics. In the NMOS digital regime, we report a very high room temperature on/off current ratio (I<sub>ON</sub>/I<sub>OFF</sub> ~ 36) in comparison to graphene-based FET devices without sacrificing the field-effect electron mobilities in graphene. By engineering the source/drain contact area, we further estimate that a higher value of I<sub>ON</sub>/I<sub>OFF</sub> up to 100 can be obtained in the device architecture considered. The device architecture presented here may enable semiconducting behavior in graphene for new electronic applications.

## **Multilayer structures of graphene and 2D materials - Electron Dynamics and Applications**

Ted Norris

University of Michigan

Abstract:

Interactions between graphene layers provide both new physics and new device concepts. We have performed ultrafast optical and THz spectroscopy of a variety of multilayer graphene systems. We have observed interlayer screening and thermal coupling via interlayer Coulomb coupling in multilayer C-face epitaxial graphene samples. Recently we have also fabricated graphene/dielectric heterostructures and stacks. We have demonstrated hyperbolic metamaterial multilayers operating in the mid-infrared, opening up new applications in both emitters and detectors. We have also developed a novel graphene double-layer heterostructure exhibiting high room-temperature infrared response, based on tunneling between the 2D layers. Prospects for extensions to new 2D systems will be discussed for optoelectronic applications.

## **Title: Electronics and Optoelectronics Using 2D Di-chalcogenides**

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Abstract:

Two dimensional transition metal di-chalcogenides present an attractive set of semiconductors that could lead to new applications for both electronics and optoelectronics. In this presentation, we shall talk about two specific examples: (i) potential for using these materials for ultra scaled digital switches and (ii) possibility of synthesizing novel heterostructures for optoelectronic applications. Within the context of these application areas, the unique opportunities provided by 2D materials and challenges for eventual technological adoption will be discussed.

## **The Research within STARnet FAME Center on van der Waals Materials**

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I will report on the research being carried out within STARnet FAME Center. The report includes a brief overview of the center, a detailed description the research of one of the four themes of FAME pertaining to van der Waals materials, and an in-depth discussion on the application potential of van der Waals materials in bio-sensing.